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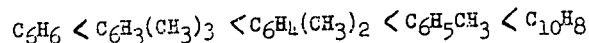
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In the opinion of L. S. Al'tman and M. S. Nemtsov, the difference between the two groups of catalysts is due to the fact that the temperature coefficients (magnitude of the change of reaction velocity with temperature) change considerably depending on the nature of the catalyst. Figures published by Al'tman and Nemtsov on the apparent energy of activation E for various catalysts and temperature coefficients calculated for temperatures of from 450 to 460°C indicate that E for Mo catalysts is several times higher than for Pd, Pt, and Ni catalysts. The temperature coefficient in the range 450-460°C fluctuates for sulfide catalysts between 1.25 and 1.54 (depending on the catalyst and the substance being hydrogenated) and for reduced catalysts (Ni, Cu, Co, and Pd) between 1.08 and 1.12.

In the course of the same investigation, Al'tman and Nemtsov have shown, by calculating the rate of hydrogenation of toluene over two catalysts (Pd and MoS_2), that even if the rate of hydrogenation over the reduced Pd catalyst at 100°C is assumed to exceed the corresponding rate over molybdenum sulfide by a factor of 100, molybdenum sulfide at 450°C will be 13 times more effective than reduced palladium.

Another difference between high-temperature hydrogenation catalysts (MoS_2 , WS_2) and low-temperature metallic catalysts (Pd, Pt, Ni) is that, with an increase of temperature, the concentration of hydrogen on the surface of catalysts of the first type (MoS_2 , WS_2) does not change greatly because of the lower heat of adsorption of hydrogen, while on catalysts of the second type (Pd, Pt, Ni) [which have a high heat of hydrogen adsorption] at low pressures and temperatures exceeding 250-300°C, the concentrations of both hydrogen and hydrocarbons drop sharply, so that a lowered reaction rate results.

In the hydrogenation of aromatic hydrocarbons which, for example, is carried out over MoS_2 at 420°C at a hydrogen pressure of 100 atmospheres, the reaction rate increases in the following sequence:



The relative activity of catalysts is illustrated in Table 1 (all tables are appended). While for liquid-phase hydrogenation both stationary and floating catalysts can be used, stationary catalysts would not be suitable for the hydrogenation of coal. The influence of the grain size of dispersed catalysts on liquid-phase hydrogenation has been investigated by I. B. Rapoport and G. Gritsevich. The results of this investigation are summarized in Table 2.

From the data in question, it follows that it is possible to work with small quantities of a colloidal catalyst which has been homogeneously embodied into the tar. When such catalysts are used, it is necessary to stir the catalyst paste continuously. In industrial practice, iron catalysts are used for hydrogenation, and their concentration in the oil often reaches a value of 20-25%.

In the process of studying hydrogenation in the presence of a highly active molybdenum catalyst, naturally it was of interest to determine the useful life of the catalyst. There is always a small quantity of carboids deposited on the surface of the catalyst, and the quantity deposited tends to reach a certain constant value. The results listed in Table 3 were obtained by reusing MoO_3 four times. It can be seen from the data listed there that the expenditure of catalyst with reference to the amount of treated tar drops with each succeeding cycle. Judging from the products obtained, the catalyst does not lose its activity. After the fourth cycle, the specific gravity of the residue did not change, while the content of carboids amounted to more than 0.1%. The content of carboids in the residue after the fifth cycle was 0.12%, while 0.47% of coal dust was introduced with the tar. The specific gravity of the residue from the reactor was 1.0000. Increase of the specific gravity of the residue may indicate occurrence of a certain amount of polymerization and condensation, but it is more likely that aromatization proceeded to some extent.

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From the results outlined above, it appears that it would be possible to recirculate repeatedly expensive catalysts [like MoO_3] after their partial withdrawal from the system subsequently to each completed cycle.

Hydrogenation of coal in the liquid phase, representing the first stage of hydrogenation, aims to convert the coal as completely as possible into oil. The product of the first hydrogenation stage is a mixture of high-molecular compounds which yields only a small quantity of substances boiling below 200°C . The hydrogenation of coal proceeds in such a manner that the product is a crude material which is suitable both for further conversion in the vapor-phase hydrogenation stage (fractions boiling at $175\text{--}300\text{--}320^\circ\text{C}$) and for production of the paste (residue boiling above $300\text{--}320^\circ\text{C}$). If the process of hydrogenation is conducted in such a way that there will be, in effect, only solution of the coal accompanied by partial hydrogenation, it will be necessary to interpose a supplementary hydrogenation of the heavy oil to obtain a product suitable for further conversion.

The liquid products obtained from coal resemble closely the high-boiling fractions of primary tar. Under the circumstances, one may assume that molybdenum and wolfram compounds, which are the most efficient catalysts for the hydrogenation of primary tar, cracking residues, and other crude raw materials, will also be perfectly suitable for the hydrogenation of coal. One drawback is the high cost of these catalysts. They must be recovered and regenerated. While the process of recovery after hydrogenation of liquid products is not too complicated, it becomes highly complicated when treatment of the ash residue resulting after hydrogenation of coal is involved. For this reason, many investigations have been devoted to the study of cheap catalysts which would not have to be recovered.

I. B. Rapoport, M. Sudzilovskaya, and A. Khudyakova tested a number of catalysts on various fossil combustibles which were both of the sapropelitic and humus types. The experiments were carried out in an autoclave equipped with a stirrer (250 rpm). A paste with the composition 1:1 was used and 1% of catalyst was added during the preparation of the paste. Some of the results of this work are cited in Table 4. According to these results, the most active catalyst is MoS_3 , both in the pure state and with the addition of activators NiO , CaO , RO [not further identified], and others. MoO_3 was also found to be pretty good, although according to the British experimental station for fuel testing at Billingham, MoO_3 is a less active catalyst. The yields of liquid products obtained in hydrogenation with $\text{Sn}(\text{OH})_2$ show that this catalyst is less active than MoS_3 and other, mixed catalysts. This must be due to the method of preparing $\text{Sn}(\text{OH})_2$, because the identical catalyst, when prepared differently, was previously shown to have an activity practically as high as that of molybdenum catalysts.

Some of the most active catalysts were also tested on other coals, and analyses of the liquid products were carried out. The results of this check are shown in Table 5. From these results, it follows that with the most active catalysts MoS_3 and $\text{MoS}_3 + \text{RO}$ a higher yield of hydrogenation products results, and that these products have a lower specific gravity, while containing less asphaltene.

As far as substitution of molybdenum catalysts with less expensive materials is concerned, results based on work carried out in recent years are listed in Table 6. The results listed there show that when the molybdenum sulfide catalyst is replaced by a chromium catalyst, corresponding results are obtained only when a much higher quantity of the latter is used. The use of a mixture of ferrous oxide and ferric oxide necessitates raising the concentration of the catalyst to 5%, but the result is still inferior to that obtained with either molybdenum sulfide or a chromium catalyst.

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Sulfur-containing iron catalysts have a higher activity than iron oxides. To obtain with the former an effect approaching that of MoS_3 , the addition of a quantity exceeding several times that of MoS_3 is necessary. Raising of the hydrogen pressure from 200 to 700 atm permits hydrogenation to be conducted with iron catalysts just as effectively as with MoS_3 , under reduction of the expenditure of iron catalyst up to a certain stage.

At German plants, dispersed iron catalysts were used for hydrogenation in the liquid phase. Ferrosulfuric oxide and iron sulfate have received the widest acceptance. The first substance is a by-product of aluminum production and contains 35% of iron. Iron sulfate was used in combination with sodium sulfide. These catalysts were used in a high state of dispersion for the hydrogenation of tars and coal.

According to K. Gordon (Chemical Age, 761-795, 1946), iron catalysts cannot be used at pressures of 200-300 atm. Actually, the answer to the question as to whether iron catalysts can or cannot be used at 200-300 atm depends on the chemical composition of the coal. Lignites and recently formed coals liquefy very well in the presence of iron catalysts at 200-300 atm. Geologically older coals, which require pressures up to 700 atm for hydrogenation, liquefy with great difficulty at 200-300 atm in the presence of iron catalysts. At 700 atm, however, the process of liquefaction proceeds effectively enough even in the presence of iron catalysts.

At present, iron catalysts are used industrially in the liquid-phase hydrogenation of untreated tars.

In the other stages of industrial hydrogenation (intermediate hydrogenation and final conversion into gasoline), stationary catalysts deposited on activated aluminum oxide and consisting of wolfram sulfide or wolfram sulfide containing nickel sulfide are used. Specially prepared molybdenum catalysts are also in use.

Fission in Vapor-Phase Hydrogenation Stage (Chapter 10c, pp 244-246)

As far as cracking catalysts are concerned, they must show the following characteristics: (1) high activity, (2) a high degree of stability in prolonged use, and (3) low sensitivity to poisoning. In regard to the efficiency of this type of catalysts, M. S. Nemtsov compiled the data of Table 7, which were supplemented in this instance by adding data taken from German industrial practice (the last two lines of Table 7). The efficiency (volumes of gasoline per volume of catalyst per hour) of the Standard Oil Company [of New Jersey's] Catalysts B and C is 2.4-2.7 times higher than that of the same company's Catalyst A. The efficiency of German industrial catalysts is 1.2-1.7 times lower than that of the US Catalyst C. A comparison of GIVD (State Scientific Research Chemical Institute of High Pressures) catalysts with the best US Catalyst C shows that the efficiency of GIVD No 881 is 2.5 times higher and that of GIVD No 79 is 1.8 times higher than that of Catalyst C. The efficiency of low-temperature Catalyst GIVD No 196 is 1.6 times higher than that of the German low-temperature catalyst tested.

Low-temperature catalysts are of especial interest, because their application permits an increase of the gasoline yield up to 115-120% by volume of the starting crude material.

The chemical composition of the crude material used in the vapor-phase hydrogenation has an effect on the composition of the resulting gasoline. Distillates with a high alkane content yield gasolines consisting chiefly of alkanes, while distillates which contain cyclic hydrocarbons yield gasolines containing cycloparaffins and aromatic hydrocarbons. The same situation exists in regard to crude materials obtained from coal. Distillate fractions obtained from boghead

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coals yield gasolines having a high content of alkanes. On the other hand, distillate fractions obtained from ordinary coal are converted into gasolines that have a high content of cycloparaffins and aromatics. Some figures illustrating this relationship are given in Table 8.

Naturally, gasolines obtained from a paraffinic crude material will have a lower octane number than those derived from crude material with a high content of cyclic hydrocarbons. Gasolines of practically identical composition are obtained from both types of crude material when treatment with the aid of an aromatizing catalyst is applied: a product containing 50-70% of aromatic hydrocarbons is then obtained from gasoline of any chemical composition.

[Appended tables follow.]

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Table 1. Results of the Hydrogenation of Generator Tar With Various Catalysts

Conditions of experiments: temperature, 410°C; constant working pressure, 150 cm;
weight of tar charged into apparatus, 550 g; quantity of catalyst, 1.3%

Catalyst	Rel Duration of Hydrogenation	Hydrogen Chemically Combined in Course of Process (%)	Sp Gr of Hydrogenated Product	Distillation (yield in %)			
				Fraction Boiling Below 200°C	Fraction Boiling Below 300°C	Residue	Losses
NiS	1.0	1.56	1.015	5.30	25.30	68.30	1.10
MoO ₃	2.6	2.08	0.9900	6.20	27.10	64.40	2.30
MoS ₃	2.2	2.42	0.9646	12.57	32.40	54.98	0.05
SnS	3.2	2.42	--	7.80	30.45	60.50	1.25
MoS ₂ + SnS	3.7	2.59	0.9680	9.15	30.00	53.00	2.35
Same	3.7	2.42	0.9780	7.60	30.00	61.50	0.90
Same	2.2	1.07	0.9960	7.15	25.10	63.50	2.25
Same	3.0	2.20	0.9800	10.40	32.60	55.00	2.00
MoS ₃ + CaO	1.6	2.06	0.9783	6.03	28.17	65.26	0.54
MoS ₃ + NiO	2.0	2.42	0.9681	8.95	31.77	53.44	0.84
MoS ₃ + ThO ₂	1.9	2.38	0.9763	8.50	29.09	61.54	0.57
MoS ₃ + RO	1.4	2.20	0.9820	7.17	29.87	62.44	1.02

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Table 2.. Effect of the Particle Size of the Catalyst MoO₂ on the Hydrogenation of Barzass Tar

Temp (°C)	Particle Size of Catalyst (fraction between the mesh sizes corresponding to the following number of holes per sq cm)	Expenditure or Catalyst in Wt (%)	Distillation (yield in % based on crude material)		Carboids (%)	Sp Gr of Residue	Iodine No of Fraction Boiling Above 300°C
			Fraction Boiling Below 200°C	Fraction Boiling Below 250°C			
431	270-900	0.05	16.65	17.00	0.30	--	23.80
428	270-900	0.005	19.40	25.00	Large quantity	--	--
431	900-2,500	0.10	14.70	20.00	0.12	0.9940	14.37
437	900-2,500	0.05	20.00	25.20	Large quantity	1.0003	19.65
426	4,900-6,400	0.10	14.65	19.75	0.08	0.9569	--
428	10,000	0.10	17.10	18.50	0.10	0.9569	--
430	10,000	0.05	17.80	23.20	0.12	0.9680	30.12
431	10,000	0.005	17.60	22.20	0.09	0.9750	38.20
431	10,000	0.0005	--	--	Large quantity	1.0015	26.33
433	Colloidal cata- lysts	0.05	14.70	24.25	Traces	0.9668	20.00
433	Same	0.005	12.48	19.45	0.30	0.9860	--
431	Same	0.0005	12.72	22.00	1.26	0.9989	--

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Table 3. Effect of Repeated Recirculation of Catalyst on Hydrogenation Process

Temp (°C)	Expenditure of Catalyst in % Referred to Tar	Distillation (yield in % referred to pressure distillate)			Characteristics of Fractions Boiling Above 300°C	
		Fraction Boiling Below 200°C	Fraction Boiling Below 250°C	Fraction Boiling Above 250°C	Iodine No	Sp Gr
408	0.05	12.80	20.60	66.40	28.00	0.9329
435	0.026	17.90	45.55	56.05	22.67	0.9541
434	0.0146	14.50	35.15	45.58	34.40	0.9542
431	0.0088	17.96	30.52	49.76	26.70	0.9414

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Table 4. Effect of Catalysts on the Hydrogenation of Chermkhovo ("Chermkhovskiy") Coal

Conditions of experiments: temperature, 400°C; initial hydrogen pressure, 80 atm; duration, 60 min;
quantity of catalyst, 1%

Type of Crude Material	Catalyst Used	Yield in % of Combustible Mass of Paste			Expenditure of Hydrogen in % Referred to Combustible Mass of Paste	Conversion % Calculated on Basis of Ash of Residue
		Liquid Products	Combustible Mass of Solid Residue	Gases Without Hydrogen		
Chermkhovo coal from main stratum and heavy tar fractions (1:1)	SnS + MoS ₂	92.63	--	--	--	92.99
	MoO ₃ + Fe ₂ O ₃	89.95	--	--	--	92.46
	MoS ₃	86.53	--	--	--	--
	MoS ₃ + Fe ₂ O ₃	82.94	--	--	--	--
	Sn(OH) ₂ + MoS ₃	81.98	--	--	--	79.10
	SnS	74.23	--	--	--	75.99
	Sn(OH) ₂	72.32	--	--	--	94.12
Chermkhovo coal from sump stratum and heavy tar fractions (1:1)	MoS ₃ + NiO	86.44	2.60	4.44	2.62	93.67
	MoS ₃ + CaO	86.81	2.84	7.86	2.34	93.49
	MoS ₃ + RO	82.53	2.92	5.84	2.68	92.39
	MoO ₃	84.43	3.43	7.62	2.42	86.40
	Nickel oleate	79.04	6.14	9.19	1.74	75.47
	ZnO	78.46	11.04	6.16	1.81	64.41
	Iron oleate	69.20	16.02	--	--	62.78
	(Without a catalyst)	68.98	16.82	6.86	0.79	

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Table 5. Effect of Catalysts on Hydrogenation of Artemovsk and Minusinsk Coals

Conditions of experiments: temperature, 400°C; initial pressure of hydrogen, 100 cm; duration, 180 min; quantity of catalyst, 1%

<u>Crude Material</u>	<u>Catalyst</u>	<u>Yield of Liquid Product (%)</u>	<u>Content of Asphaltenes in Organic Mass of Discharged Product (%)</u>	<u>Yield of Organic Substance of Residue (%)</u>	<u>Sp Gr of Hydrogenation Products</u>
Paste from Artemovsk coal and heavy oil	MoS ₃ + RO	78.7	9.8	5.0	1.023
Same	MoS ₃	76.7	--	6.9	1.024
Same	Sn(OH) ₂	74.8	--	16.0	1.053
Same	Fe ₂ O ₃	71.1	14.7	27.8	1.065
Same	(Without a catalyst)	60.1	--	43.5	1.020
Paste from Minusinsk coal and heavy oil	MoS ₃ + RO	81.5	18.0	4.8	1.114
Same	MoS ₃ + Fe ₂ O ₃	79.9	20.4	5.5	1.106
Same	MoS ₃	78.0	20.8	5.2	1.117

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Table 6. Effect of Various Catalysts on Hydrogenation of Cherekhovo Coal

Conditions of experiments: temperature, 400°C; initial pressure of hydrogen, 90 cm;
duration, 90 min

Catalyst	Quantity of Catalyst (%)	Yield in % Referred to Combustible Mass of Paste		Expenditure of Hydrogen in % Referred to Paste	Conversion in % Based on Ash of Solid Residue	Content of Asphaltenes in % Referred to Total Liquid Product
		Liquid Product	Combustible Mass of Solid Residue			
MoS ₃	1.0	84.26	3.27	1.76	92.68	8.52
Chromium	0.5	77.98	6.50	1.92	85.43	7.
"	1.0	79.30	4.95	--	88.91	6.33
"	3.0	81.85	3.62	1.72	91.88	7.65
Ferrous and ferric oxide	1.0	76.70	9.39	--	--	7.84
Same	3.0	78.84	8.09	1.49	81.94	7.66
Same	5.0	80.27	8.22	--	--	--

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Table 7. Efficiency of USSR Catalysts Compared With US and German Catalysts

Crude Material	Final Bp of Crude Material (°C)	Sp Gr of Crude Material	Catalyst	Temp in Reaction Zone (°C)	Efficiency Calculated on Basis of Gasoline Yield (vol of gasoline per vol of catalyst per hr)	
					Gasoline Boiling Below 160°C	Gasoline Boiling Below 175°C
		15 d 15				
Old GIVD USSR catalysts on pilot-plant installations						
Kerosene distillate	336	0.822	MoS ₂ on silica gel	540	0.35	0.42
Groznyy cracking phlegm	>350	0.865	MoS ₂ , Cr ₂ O ₃ , ZnO	540	0.35	0.43
Green oil	>350	0.925	MoS ₂ , Cr ₂ O ₃ , ZnO	540	0.11	0.13
New GIVD USSR catalysts on pilot-plant installations						
Kerosene distillate	323	0.830	No 92	470	--	1.60
Baku kerosene dis- tillate	330	0.850	No 196	420-425	1.22	1.58
Groznyy kerosene distillate	280	0.804	No 79	500	2.30	--
Emba kerosene dis- tillate	347	0.841	No 81	430	0.45	--
Emba kerosene dis- tillate	347	0.841	No 81	465	1.55	--
Emba kerosene dis- tillate	347	0.841	No 81	500	3.26	--
Green oil (after pre- liminary hydrogenation)	330	0.883	No 53	480	--	2.36

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Table 7 (Contd)

Crude Material	Final Bp of Crude Material (°C)	Sp Gr of Crude Material	Catalyst	Temp in Reaction Zone (°C)	Efficiency Calculated on Basis of Gasoline Yield (vol of gasoline per vol of catalyst per hr)	
					Gasoline Boiling Below 160°C	Gasoline Boiling Below 175°C
		15 d 15				
Data from industrial installations of Standard Oil Co, US						
Gas oil	329	0.855	A	430-540	0.36	0.43
" "	329	0.855	B	430-540	0.66	1.03
" "	329	0.855	C	430-540	0.98	1.15
Blended cracking gas oil	360	0.855	C	430-540	0.72	0.85
Light mid-continent gas oil	326	0.821	C	430-540	1.27	1.49
Experimental data from Baton Rouge [Standard Oil Co of NJ]						
Blended Virginia [sic] and cracking gas oil	362	0.904	Low-temperature catalyst	345-430	1.28	1.37
Heavy cracking gas oil	296	0.905	Low-temperature catalyst	445-430	1.05	1.20
Data from German industrial installations						
Lignite distillate	300-320		~10% of WS ₂ + 90% of diatomaceous earth	380-430	0.5-0.65	--
Coal distillate	300-320		~10% of WS ₂ + 90% of diatomaceous earth	380-430	up to 0.83	--

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Table 8. Characteristics of Gasolines Obtained From Various Types of Crude Material

(M. S. Nemtsov, I. B. Rapoport, and M. Pir)

Crude Material	Characteristics of Crude Material			Characteristics of Gasoline						
	Distills in %		Sp Gr d ₁₅ ¹⁵	Final Bp (°C)	d ₂₀ ²⁰	Olefins	Aromatics	Cyclo-paraffins	Alkanes	Octane No
	Below 300°C	Below 350°C								
Groznyy cracking phlegm	67.4	93.8	0.861	152	0.721	5.5	12.5	28.0	54.0	46.5
Groznyy cracking phlegm plus recirculated oil	--	--	--	163	0.741	5.0	22.0	23.0	50.0	53.0
Groznyy paraffinic solar oil	--	--	0.854	161	0.725	3.0	9.0	33.0	55.0	58.0
Green oil from pyrolysis process	84.8	--	0.922	178	0.769	3.0	37.5	33.0	26.5	73.0
Green oil from pyrolysis process plus recirculated oil	--	--	--	176	0.806	3.0	55.0	32.0	10.0	80.0
Gusev peat tar	--	--	--	157	0.781	2.5	40.0	39.0	18.5	71.5
Gusev peat tar plus recirculated oil	--	--	--	160	0.722	4.0	31.5	33.5	31.0	68.0
Crude material used in operation (coal distillate plus recirculated oil)	84.9	99.0	0.925	160	--	--	--	--	--	68.0
Crude material used in operation (distillate from bog-head coal mined in Moscow region plus recirculated oil)	--	99.0	0.830	160	--	--	--	--	--	56.5
Coal distillate	--	--	--	160	0.790	2.1	44.4	40.7	12.8	70.0

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Table 8 (Contd)

Crude Material	Characteristics of Crude Material			Characteristics of Gasoline						
	Distills in %		Sp Gr @ 15.5	Final Bp (°C)	d 20	Olefins	Aromatics	Cyclo-paraffins	Alkanes	Octane No
	Below 300°C	Below 350°C								
Crude material used in operation (coal distillate plus recirculated oil)	--	--	--	160	0.754	0.7	32.4	42.2	24.7	67.5
Estonian shale oils	--	--	--	185	0.732	1.0	9.0	31.5	58.5	66.0
Scotch shale oils	--	--	--	187	0.712	1.0	5.0	18.5	75.5	65.0

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